substituent in the nucleophile, substrate and leaving group respectively, and N and L, the nucleophile and leaving group respectively.
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Synthesis of (Z)-, and (E)-8-Dodecen-1-yl Acetate, The Sex Pheromone of the Oriental Fruit Moth, Grapholitha Molesta by Stereochemical Control in Wittig Olefination

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Stereochemical control of the Wittig reaction of the primary aldehyde, 8-acetoxyoctan-1-al (**7**) with the nonstabilized alkylide, triphenylphosphonium n-butylide (**6**), was achieved by controlling the reaction conditions including solvent, temperature and inorganic salts. These conditions can be applied to the direct synthesis of the mixture of (Z)-, and (E)-8-dodecen-1-yl acetate, the sex pheromone of the oriental fruit moth, *Grapholitha molesta*. The primary aldehyde, 8-acetoxyoctan-1-al (**7**) was synthesized from 1,8-octanediol which is cheap and readily available.

Introduction

The sex pheromone of the oriental fruit moth, a major economic pest of apple, peach, and other fruits in Korea[1] was identified as (Z)-8-dodecen-1-yl acetate (**1**) by Roelofs *et al.*[2] in 1969. Later, the requirement for attractancy of an isomeric mixture containing a samll amount of (E)-8-dodecen-1-yl acetate (**2**) was demonstrated.[3] In 1979, Carde *et al.*[4] isolated three volatile components from gland of Grapholitha molesta Busk virgin females and identified as (Z)-, and (E)-8-dodecen-1-yl acetate and (Z)-8-dodecen-1-ol (**3**). It was reported[5] that dodecanol (**4**) act as a synergist and dodecenyl acetate (**5**) act as an inhibitor (Figure 1).

Catches of the oriental fruit moth males at traps baited with (Z)-8-dodecen-1-yl acetate were much influenced by small amounts of the (E)-isomer. Even if the biological activity depends on place and climate, the ratio of (Z)-to (E) at 6~15% gave the best capture. 93% (Z)-and 7% (E)-8-dodecen-1-yl acetate, the synthetic pheromone was known as Orfralure.[6]

The oriental fruit moth, *Grapholitha molesta*, is not attracted at all by light traps, therefore, survey of the trend of their outbreak in the field is difficult.[7] Seasonal fluctuation of this pest can be traced by using sex pheromone traps. The forecasting by using traps baited with a synthetic sex pheromone will con-

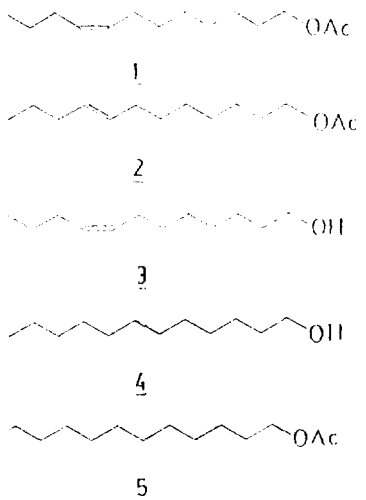


Figure 1.

tribute to the saving of labour required for the survey made by light trap and will bring in an increased accuracy in forecasting and thus to the timely application of pesticides.

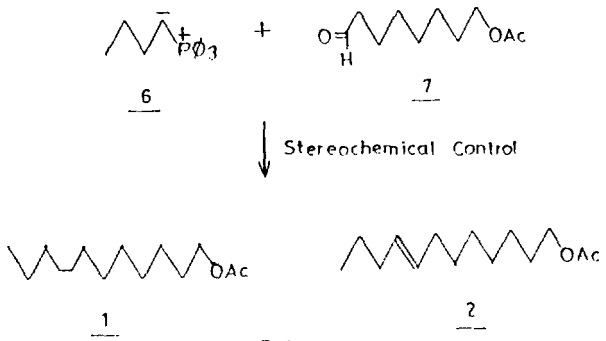
Several syntheses of (Z)-and (E)-8-dodecen-1-yl acetate, the sex pheromone of the oriental fruit moth have been reported.[8]

Institute of Agricultural Sciences in Suwon, Korea need a fair amount of the pheromone of the oriental fruit moth to conduct field test experiments. We therefore undertook to develope a practical method for the synthesis of the mixture of the (Z)-and (E)-8-dodecen-1-yl acetate.

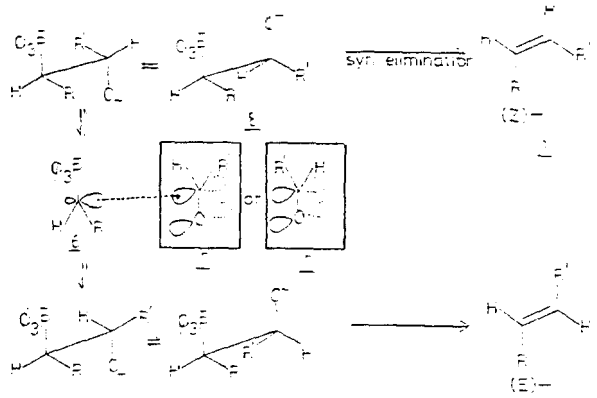
Results and Discussion

Although (Z)-isomer (**1**) and (E)-isomer (**2**) can be prepared separately by conventional routes via acetylenic intermediate,[9] we decided to prepare the required mixture of (Z)-and (E)-isomers by a single synthetic scheme (Scheme 1) involving stereochemical control of the Wittig olefination reaction.

Generally, the effect of the reaction conditions on the stereochemical outcome of the Wittig reaction has been extensively studied.[10,11] Thus it is known that, when saturated aliphatic nonstabilized triphenylphosphonium ylides react with primary aliphatic aldehydes in nonpolar solvent such as benzene or THF at 0°C in the absence of inorganic ions ("salt-free"), predominantly (>90%) (Z)-olefins are isolated from the Wittig condensations.[10a-d] The same result is obtained, with nonstabilized alkylides and aliphatic aldehydes, in the presence of lithium salts if the reaction is carried out in a dipolar aprotic solvent such as dimethylformamide,[10h] dimethyl sulfoxide[12a] or hexamethylphosphoramide.[12b,c] In nonpolar solvents, the stereochemistry of the olefin product is dependent on the nature of the inorganic salts present such as LiBr or LiCl.[10a-c] Schlosser[12] tentatively interpreted these results, for nonpolar solvents, by assuming that in "salt-free" solution, the alkylide and aliphatic aldehyde react essentially irreversibly to give a "betaine"[13] (**8**) with predominantly the erythro configuration (and hence (Z)-olefin product), with the rate of decomposition of the "betaine" to the product being slower than its rate of formation. Schlosser postulated that, in the presence of lithium salts, the initial erythro-"betaine" adduct (**8**) is partially converted to the thermodynamically more stable thereo-"betaine" (**9**) via reversion to the starting aldehyde and ylide, resulting in an increase in the portion of the (E)-isomer in the olefin product (Scheme 2). Whether or not the relatively unstable Wittig intermediate derived from an aliphatic aldehyde (**7**) and a nonstabilized ylide (**6**) could be partially equilibrated, the reaction could be controlled to give different mixtures of cis and trans olefin (**1** and **2**).



Scheme 1

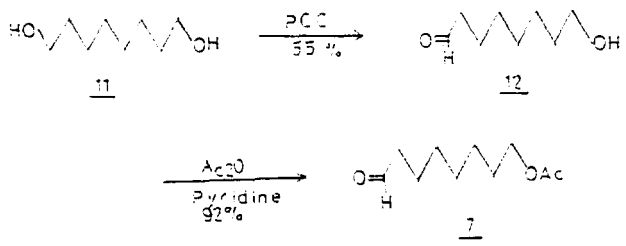


Scheme 2

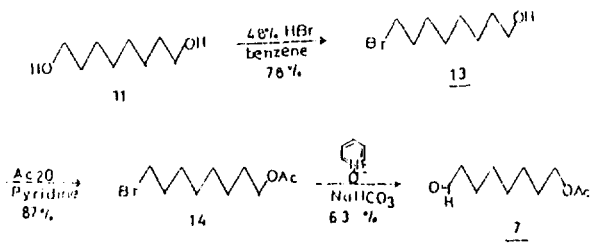
Table 1. Reaction of 8-acetoxyoctan-1-al (7) with Triphenyl Phosphonium n-butylide (6)

entry	reaction condition						Product	
	ylide formation				olefin formation		isomer ratio[a]	isolated yield[c]
	base	solvent	temp	time(hr)	temp	time(hr)	**1 : 2**	%
1	nBuLi, (12-crown-4[b])	benzene,	25°C	1	25°C	2	100 : 0	58%
2	KH	DMSO	25°C	2	25°C	2	98 : 2	68%
3	NaH	DMSO	75°C	1	25°C	2	94 : 6	68%
4	nBuLi	benzene	25°C	1	25°C	3	93 : 7	55%
5	nBuLi	DMSO	25°C	1	25°C	1	92 : 8	67%
6	LiN-$(SiMe_3)_2$	THF/HMPA	−78°C	3	0°C	3	76 : 24	68%
7	nBuLi	THF	−25°C	1	25°C	1	65 : 35	52%
8	tBuOK	THF	25°C	1/2	25°C	2.5	47 : 53	67%

[a] The isomer ratio was determined by gas chromatography (Cabowax 20M, 16 feet 1/8 inch, 200°C). [b] A catalytic amount was used. [c] The yields have not been optimized.



Scheme 3



Scheme 4

Table 1 summarizes our results on the effect of solvent, temperature, inorganic salts, and base on the isomer ratio in the product, from the Wittig reaction of the aliphatic aldehyde (**7**) with n-butylide (**6**). In the "salt-free" condition by adding a catalytic amount of 12-crown-4 (entry 1), only cis olefin was formed. When the ylide (**6**) (prepared from phosphonium bromide salt with KH) was allowed to react in DMSO with the aldehyde (**7**) at 25°C, then 98:2 ratio of **1**:**2** was afforded (entry 2 in Table 1). When NaH was used instead of KH, a 94:6 mixture of **1** and **2** was obtained (entry 3). With n-BuLi as bases in benzene and DMSO, the Wittig reaction gave 93:7 and 92:8 mixtures of **1** and **2** (entry 4,5), of which ratios are in the range of inhanced pheromone activity. A normal Wittig reaction in THF in the presence of lithium bromide (entry 7) gave 65:35 ratio of **1**:**2**. In the presence of HMPA (entry 6), 76:24 mixture of (Z)- and (E)-isomer was obtained. In the presence of KOtBu in THF, by the partial equilibration of the Wittig intermediate, a 47:53 ratio of **1** and **2** was obtained (entry 8).

8-Acetoxyoctan-1-al (**7**), the key intermediate, was easily synthesized from 1,8-octanediol, which is cheap and readily available. Oxidation[14] of 1,8-octanediol (**11**) with 1 equivalent of PCC gave 8-hydroxyoctan-1-al (**12**). Acetylation with acetic anhydride afforded 8-acetoxyoctan-1-al (**7**) (Scheme 3). Alternatively, 1,8-octanediol was subjected to monobromination[15] to yield 8-bromooctan-1-ol (**13**), which was subsequently acetylated to give 8-bromooctan-1-yl acetate (**14**). Pyridine N-oxide oxidation[16] of 8-bromooctan-1-yl acetate (**14**) afforded 8-acetoxyoctan-1-al (**7**) (Scheme 4).

Experimental

Infrared spectra were recorded with Shimadzu IR-440 spectrophotometer. ^{1}H-NMR spectra were taken on a Bruker WP 80 SY 80 MHz NMR spectrophotometer, using tetramethylsilane as an internal standard. Gas chromatogams were obtained on a Spectra-Physics 7100 gas chromatography with Carbowax 20M Column (16 feet 1/8 inch, 200°C). Preparative thin-layer chromatography (PTLC) was in general carried out on 20cm × 20cm glass plates coated with × 1mm of Merck silicagel PF-254. All solvents and liquid compounds were distilled before use.

8-Hydroxyoctan-1-al (12). To a stirred solution of 1,8-octanediol (**11**) (0.73g) in methylene chloride (4m*l*) was added PCC (1.1g) in methylene chloride (5m*l*). The mixture was stirred at room temperature for 2hrs. To the reaction mixture, ether (30m*l*) was added and filtered through alumina pad. The filtrate was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The organic solution was concentrated in vacuo to give 8-hydroxyoctan-1-al (**12**) (0.40g, 55%); IR (neat) 3400, 2900, 2750, 1730 cm^{-1}; NMR($CDCl_3$) δ 1.2-1.7 (m, 10H), 2.4 (t, 2H), 3.7 (t, 2H), 9.8 (t, 1H).

8-Acetoxyoctan-1-al (7). To a stirred solution of 8-hydroxyoctan-1-al (**12**) (0.50g) in dry pyridine (5m*l*) was added acetic anhydride (0.50g) at room temperature. The mixture was stirred overnight at room temperature, poured into distilled water (15m*l*) and extracted with ether. The ether solution was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Concentration in vacuo gave 8-acetoxyocatan-1-al (**7**) (0.60g, 92%); IR (neat) 2900, 2750, 1730 cm^{-1}; NMR ($CDCl_3$)δ 1.2-1.7 (m, 10H), 2.1 (s, 3H), 2.4 (t, 2H), 3.7 (t, 2H), 9.8 (t, 1H).

8-Bromooctan-1-ol (13). To a stirred solution of 1,8-octanediol (**11**) (1.0g) in benzene (40m*l*) was added 48% HBr. The mixture was heated at reflux while trapping water using a Dean-Stark separator. After benzene was evaporated and extracted with ether and washed with 6N NaOH, 10% HCl, and then saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was distilled on Kugelrohr (110°C, 3mmHg) to give 8-bromooctan-1-ol (**13**) (1.3g, 78%); IR (neat) 3500, 2900, 1050 cm^{-1}; NMR ($CDCl_3$)δ 1.2-2.0 (m, 13H), 3.4 (t, 2H), 3.6 (t, 2H).

8-Bromooctan-1-yl acetate (14). To a stirred solution of 8-bromooctan-1-ol (**13**) (0.26g) in dry pyridine (1.8m*l*) was added acetic anhydride (1.8g). The mixture was stirred overnight at room temperature, and poured into water (10m*l*), and extracted with ether. The ether layer was washed with 1N-HCl, saturated $NaHCO_3$, and then saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give 8-bromooctan-1-yl acetate (**14**) (0.27g, 87%); IR (neat) 2900, 1730, 1230, 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.2-1.5 (m, 12H), 2.1 (s, 3H), 3.4 (t, 2H), 3.6 (t, 2H).

8-Acetoxyoctan-1-al (7). To a stirred solution of 8-bromooctan-1-yl acetate (0.17g) in toluene (3m*l*) was added pyridine N-oxide (0.11g) and $NaHCO_3$(0.10g) under N_2 atmosphere. The mixture was heated at reflux at 110°C for 4hr. After reaction, the reaction mixture was cooled and poured into ice water and extracted with pet ether. The ether layer was concentrated in vacuo to give 8-acetoxyoctan-1-al (**7**) (80mg, 63%); IR (neat) 2900, 2750, 1730 cm^{-1}; NMR($CDCl_3$) δ 1.2-1.7 (m, 10H), 2.1 (s, 3H), 2.4 (t, 2H), 3.7 (t, 2H), 9.8 (t, 1H).

A: n-BuLi in Benzene in the presence of 12-crown-4 (Entry 1, Table 1). To a stirred solution of n-butyltriphenylphosphonium bromide (0.43g) in dry benzene (5m*l*) at room temperature under N_2 atmosphere was added n-BuLi (1.55M, 0.92m*l*) at 25°C and stirred for 1hr at 25°C. To the mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in benzene (3m*l*) and was added 12-crown-4 (a catalytic amount) at room temperature and stirred for 2hr. The reaction mixture was

poured into ice water and then extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (42mg, 58%) in the ratio of 100:0 (determined by gas chromatograhy); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

B: Potasium Hydride in Dimethyl Sulfoxide (Entry 2, Table 1). To oil-free KH (55mg) was added dry DMSO (1.5m*l*) and stirred at 25°C for 1hr. To this mixture was added n-butyltriphenylphosphonium bromide (0.43g) at room temperature and stirred for 2hr at room temperature. To this reaction mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in DMSO (0.80m*l*) and stirred for 2hr at room temperature. The reaction mixture was poured into ice water and then extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (50mg, 68%) in the ratio of 98:2 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

C: Sodium Hydride in Dimethyl Sulfoxide (Entry 3, Table 1). To oil-free NaH(0.05g) was added dry DMSO (2m*l*) and stirred at 75~80°C for 1hr. To this mixture was added n-butyltriphenylphosphonium bromide (0.35g) at room temperature and stirred for 2hr at room temperature. To this reaction mixture was added 8-acetoxyoctan-1-al (**7**) (48mg) in dry benzene (5m*l*) and stirred for 3hr at room temperature. The reaction mixture was poured into ice water and extracted with ether. The ether layer was washed with water and then saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was separated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (40mg, 68%) in the ratio of 94:6 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

D: n-BuLi in Benzene (Entry 4, Table 1). To a stirred solution of n-butyltriphenylphosphonium bromide (0.43g) in dry benzene (5m*l*) at room temperature under N_2 atomsphere was added n-BuLi (1.55m, 0.92m*l*) at 25°C and stirred for 1hr at 25°C. To the mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in benzene (3m*l*) at room temperature and stirred for 2hr. The reaction mixture was poured into ice water and extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (40mg, 55%) in the ratio of 93:7 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H) 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

E: n-BuLi in Dimethyl Sulfoxide (Entry 5, Table 1). To a stirred solution of n-butyltriphenylphosphonium bromide (0.43g) in dry DMSO (5m*l*) at room temperature under N_2 atmosphere was added n-BuLi (1.55M, 0.92m*l*) at 25°C and stirred for 1hr at 25°C. To the mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in DMSO (3m*l*) at room temperature and stirred for 1hr. The reaction mixture was poured into ice water and extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (49mg, 67%) in the ratio of 92:8 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

F: $LiN(SiMe_3)_2$ in THF and HMPA (Entry 6, Table 1). To a stirred solution of n-butyltriphenylphosphonium bromide was added $LiN(SiMe_3)_2$ (0.13g) and stirred for 3hr under a was added $LiN-(SiMe_3)_2$ (0.13g) and stirred for 3hr under a N_2 atmosphere. To the mixture was added 8-acetoxyoctan-1-al (**7**) (48mg) in THF (2.3m*l*) and stirred at 0°C for 4hr. The reaction mixture was poured into ice water and then extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentraed in vacuo. The crude product was separated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (40mg, 68%) in the ratio of 76:24 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

G: n-BuLi in THF (Entry 7, Table 1). To a stirred solution of n-butyltriphenylphosphonium bromide (0.42g) in dry THF (5m*l*) at room temperature under N_2 atmosphere was added n-BuLi (1.55M, 0.98m*l*) at -20°C and stirred for 1hr at -20°C. To the mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in THF (2.7m*l*) at room temperature and stirred for 1hr. The reaction mixture was poured into ice water and then extracted with ether. The ether layer was washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to ive (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (40mg, 52%) in the ratio of 65:35 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2~1.7 (m, 16H), 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

H: tBuOK in THF (Entry 8, Table 1). To a stirred solution of tBuOK (60mg) in dry THF (2m*l*) was added and stirred at room temperature for 10min. To this mixture was added n-butyltriphenylphosphonium bromide (0.43g) at room temperature and stirred for 1/2hr at room temperature. To this reaction mixture was added 8-acetoxyoctan-1-al (**7**) (60mg) in dry THF (1m*l*) and stirred for 3hr at room temperature. The reaction mixture was poured into ice water and extracted with ether. The ether layer was washed with water and then saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was seperated by preparative tlc plate using ethyl acetate as eluent (R_f = 0.85) to give (Z)- and (E)-8-dodecen-1-yl acetate (**1** and **2**) (49mg, 6%) in the ratio of 49:53 (determined by gas chromatography); IR (neat) 2900, 1750, 1460, 1240, 1040 cm^{-1}; NMR($CDCl_3$) δ 0.9 (t, 3H), 1.2-1.7 (m, 16H) 2.1 (s, 3H), 3.7 (t, 2H), 5.4 (t, 2H).

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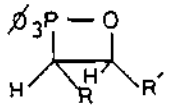

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Figure 2.

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